Studies on the Organic Molecular Compounds. Part V. On the Formation of Some Crystalline Organic Molecular Compounds.

By Chiro SHINOMIYA.

(Received May 20, 1940.)

The formation of "Molecular lattice" construction in the crystalline state is not confined to ordinary organic compounds but organic molecular compounds with fairly simple molecular ratio of parent components, probably also form certain regularly ordered crystal lattices. Zachariasen(1) and Robertson(2), from X ray analysis of oxalic acid dihydrate, found a unit lattice of $(CO_2H)_2$ and $2H_2O$ being regularly arranged and oriented, and Hertel (earlier but in less detail) studied the crystal lattice of aromatic-nitroaromatic molecular compounds(3).

Of the unit lattice of molecular compounds, numerous variations in the lattice type are possible, owing to the differences of the number of included molecules, their arrangement and their orientation. Although these differences may be due to the molecular structure of their components, it is nevertheless not an easy matter to treat them comprehensively and conclusively. The theories offered and experiments made with a view to solve this problem are yet too scanty, although from experimental induction and by comparing a number of organic molecular compounds very similarly constituted, it was found that the compound-formation, namely, the formation of crystalline molecular compounds, is most closely related to the configuration, particularly, to the molecular shape (as a whole) of the components. Although compound-formation in the crystalline state differs from that of the simple molecular compounds formed in the dilute solution, the former has also a regularity in structure.

The following two types of combination exist, for example, in the binary systems of naphthalene monosubstitution products with nitro compounds:

$$\text{(I)}\quad HO\cdot H_7C_{10} \cdots\cdots (NO_2)_3\cdot C_6H_3$$

$$\text{(II)}\quad C_{10}H_7\cdot NH_2 \cdots\cdots HO\cdot C_6H_2\cdot (NO_2)_3 \ .$$

It is seen that nitro radicals combine with the unsaturated carbon linkings in (I), and that hydroxyl radical combines with the substituent of naphthalene nucleus in (II), these two types being called here for convenience "the compound of the first and the second type" respectively. Some of the differences in the two types, especially, halochromic phenomenon (prominent in the first type but not in the second), has often been used as a criterion to distinguish the two types.

---

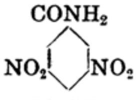
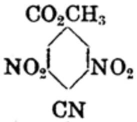
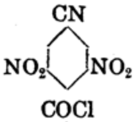
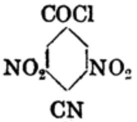
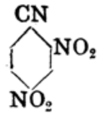
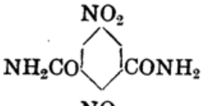
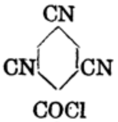
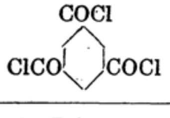
(1) W. H. Zachariasen, *Z. Kryst.*, **89** (1934), 529.

(2) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, **1936**, 1817.

(3) E. Hertel and H. Kleu, *Z. physik. Chem.*, B, **11** (1931), 59; E. Hertel and K. Schneider, *Z. physik. Chem.*, B, **13** (1931), 387.

The writer compared, chiefly in compounds Type I, the compound-formation of naphthalene monosubstitution products⁽⁴⁾ between them, and pointed out the greater tendency of compound-formation of the α-isomer and so the stronger hindering effect of the β-isomer, the results being shown in Tables 1⁽⁵⁾ and 2⁽⁶⁾.

Table 1. Molecular Compounds obtained from Solution by Bennet.

Mol ratio A : B (Melting point) τ Colour / A B [Melting point]	α-Naphthylamine	β-Naphthylamine	Naphthalene
 [183]	1 : 1 (149) 32.5 Scarlet	—	—
 [112]	1 : 1 (120) 39 Deep red	1 : 1 (90) −21 Orange	1 : 1 (80) −16 Lemon yellow
 [127]	1 : 1 (169) 80.5 Dark red	1 : 1 (113.5) −5.0 Deep red	1 : 1 (123) 19.5 Pale yellow
 [74]	—	—	1 : 1 (127) 50 Pale yellow
 [100]	m : n Strong halochromic	1 : 1 [135]* 29.1 Strong halochromic	m : n Halochromic
 [>300]	m : n Strong halochromic	m : n Strong halochromic	—
 [205]	1 : 1 (149) 21.5 Deep red	1 : 1 (107.5) −50.0 Dark red	m : n Halochromic
 [263]	1 : 1 (167) 10.5 Dark yellow	m : n Halochromic	∨ Not halochromic
 [37]	—	—	1 : 1 (101) 42.5 Almost colourless

* This system, and all those in Table 2−5, were verified by phase diagrams.

Bennet noted the following orders of diminishing tendency of substituents to promote compound-formation:

$$COCl > CO_2CH_3 > CONH_2, \quad NO_2 > CN > CO_2CH_3, \quad COCl \doteqdot NO_2, \quad \text{etc.}$$

---

(4) Part IV, This Bulletin, **15**, (1940), 281.

(5) G. M. Bennet and R. L. Wain, *J. Chem. Soc.*, **1936**, 1109.

(6) Data from the literature with writer's additional data.

Table 2. Binary Systems of Type I.

A Mol ratio A : B [Melting point] τ B	α-Naphthol	β-Naphthol
Acetophenone	1 : 1 [13] −44.9	1 : 1 U
Benzophenone	1 : 1 [38]	∨
Chalkone	∨	∨
Dibenzalacetone	2 : 1 [68] −33.3	∨
Dianisalacetone	3 : 2 [69] −40.2	3 : 2 [74] −50.8
p-Quinone	1 : 1 [100] −6.0 or 2 : 1 [120] 7.3 or 1 : 2	1 : 1 [85] −34.0 or 2 : 1 or 1 : 2
Fenchone	1 : 1 [60.5]	1 : 1 U
Antipyrine	1 : 2 [73]	1 : 1 [79.5]
Dimethylpyrone	1 : 1 [69.8] 3 : 2 [79.1]	2 : 1 [44.6] 3 : 2 [39.5]
Cineole*	1 : 1 [75]	1 : 1 [48]

* Some more cyclic ethers were synthesized, and the superior compound-formation of α-naphthol investigated (Bennet, Wain, *J. Chem. Soc.*, **1936**, 1114.).

The molecular compounds shown in Table 1, synthesized and observed by Bennet, had a halochromium similar to those of nitro molecular compounds, the order of compound-formation given by him being in good agreement with that of the value τ in Table 1. The quinones, which are very halochromic in these combinations, were investigated in a series of experiments by Pfeiffer, and proved by him to belong to this type(7). It is noteworthy that, as in the *p*-quinone, which is regarded as one of the cyclic ketones, the ketones also form more easily a compound with α- than with β-naphthol.

The substitution radical in combination Type I that showed no direct effects upon the formation of molecular compounds, ought to function as the point of contact in combination Type II, and consequently there must be here a greater tendency of compound-formation in β-position. This was actually confirmed by the data of Tables 3(6) and 4(6).

When the compounds of a binary system have substituents either the same or similar to each other, then the tendency of compound-formation diminishes to a marked degree. For example, in Table 5, the binary system was of simple eutectic type, or of a eutectic type with two solid solutions(8), or it was of a very feeble compound type.

---

(7) P. Pfeiffer, "Organische Molekülverbindungen," 2 Aufl., 282, Stuttgart (1927).

(8) The so-called "Roseboom's MKV Type" which seemed to be less compound-formable than the compound type, together with those of other solid solutions.

Table 3. Binary Systems of Type II.

Mol ratio A : B [Melting point] τ — A B	α-Naphthol	β-Naphthol
Trimethylcarbinol	1 : 2 [1] −48.0	1 : 2 [24] −33.7
Diphenylcarbinol	∨	2 : 3 [62] −27.6
Triphenylcarbinol	∨	∨
m-Aminophenol	∨	1 : 1 [99] −23.5
Aniline	1 : 1 [32] −12.9 1 : 2 [28] 0.1	1 : 1 [82] 24.1
p-Toluidine	1 : 1 [53.6] −16.3	1 : 1 [81.2] −1.7
o-Phenylenediamine	1 : 1 [60] −39.9	1 : 1 [86] −26.9
m- ,,	1 : 1 [35] −44.4	2 : 1 [114] 11.7
p- ,,	2 : 1 [110] −0.6	2 : 1 [150.5] 22.6
α-Naphthylamine	1 : 4 [43] −16.2	2 : 3 [66] −12.8
β- ,,	∨	2 : 1 [123] 5.0
Acridine	1 : 1 [116] 14.0 1 : 2 U	3 : 2 [135] 18.6 1 : 2 U
Carbazol, Azobenzene, Diphenylamine, Benzamide, Urea	∨	∨
Acetamide	∨	1 : 1 [63]
Succinimide	∨	1 : 1 [87.5]

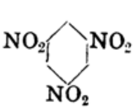
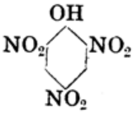
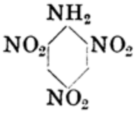
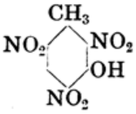
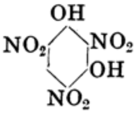
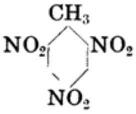
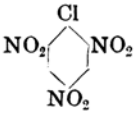
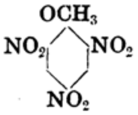
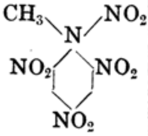
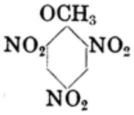
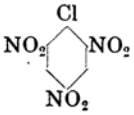
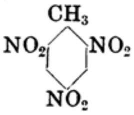
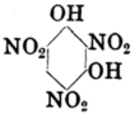
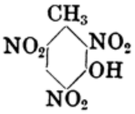
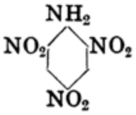
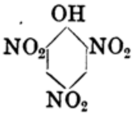
Table 4. Binary Systems of Type II.

Mol ratio A : B [Melting point] τ — A B	α-Naphthylamine	β-Naphthylamine
Trimethylcarbinol	2 : 1 [30.5] −11.3 1 : 2 [24] −9.7 1 : 6 [16] −13.0	2 : 1 [95] 13.2 1 : 2 U
Triphenylcarbinol	6 : 1 [41] −25.1	2 : 1 [D : 92] −35.5.
Diphenylcarbinol	∨	∨
Pyrogallol	2 : 1 U	2 : 1 [121.5] 3.5
Catechol	1 : 2 [43.4] −43.3 or 1 : 1	1 : 1 [77.6] −29.9
Resorcinol	1 : 1 U ?	1 : 1 [81.3] −28.7
Hydroquinol	1 : 1 U	1 : 2 [142] −8.3
Phenol	1 : 1 [28.6] −16.9	1 : 1 [83.5] 8.0
m-Aminophenol	∨	1 : 1 [D : 91] −25.5
Salicylic acid	1 : 1 U	1 : 1 U
Benzoid acid, Cinnamic acid	∨	∨
Succinic acid	∨	1 : 1 [133.5] −14.0
Acetic acid	∨	∨

The guaiacol and the three cresols are formed of exceptionally inferior compound-formation with β-naphthylamine, which has a relatively high melting point compared with the above mentioned four substances.

Naphthols and naphthylamines are believed to have an ester or salt type of combination with alcohols, amines, and acids.

Table 5. Binary Systems of *sym*-Trinitrobenzene and its Derivatives.

A *** A:B B								
	∨*	∨* or 1:1*	∨*	∨*	∨*	∨* or 2:3 D*	—	∨*
	∨**	∨**	∨ [59.5] 8%	(MKV) [50] 16%	MKV [55] 9%?	∨**	MKV [34.0] 45%	
	MKV [61.5] 35%	MKV*	MKV [72.5] 10%	MKV [55.0] 34%	MKV [65.0] 11%	2:1 [77] or 1:1*		
	1:1 [D:60]?**	∨* [58.5]	MKV [75.0] 9%	∨*	∨* or (MKV) [71.5] 11%			
	∨* or MKV [104.0] 81%	MK*	MKV	∨ [68.8]*				
	MKV [67.0] 49%	∨*	MKV [94.0] 20%					
	MKV [110.0] 67%	MKV*						
	∨**							

* Landolt, Börnstein, "Physikalisch-chemische Tabellen", 5 Aufl., **122**.

** The writer's value, with corrections (Shinomiya, Asahina, *J. Chem. Soc. Japan*, **57** (1936), 732; **58** (1937), 118.).

*** Type A—B, [Melting point or eutectic point], weight % of A in the eutectic point, are here noted.

Trinitrotoluene was found to form some molecular compounds in these combinations.

Bennet, who noticed that there was no crystalline molecular compound of picric acid with *p*-quinone(9), similarly proved *sym*-trinitrobenzene—antimony trichloride to be a simple eutectic system.

The writer showed also that the hindering effect was due to the magnitude of the substituent radicals as the result of chelation or of steric causes(4). By substituting a long aliphatic chain in the naphthalene ring, the aromatic character diminished and the characteristic aliphatic properties progressively increased(10).

Needless to say, in the case of formation of crystalline molecular compounds in the binary systems, the influence of association, not the combination of the two component molecules A—B, but of the same component molecules A—A or B—B, is also to be considered. Although this is generally not pronounced, qualitatively speaking, substitution of a radical with strong association in the α-position of naphthalene ring results especially in considerable rise in the melting point of the α-substitution product. In case that such atomic groups, for example, as $-CONH_2$, or $-CONH-$ (regarded as the most strongly associated), are introduced in the α-position, we cannot expect the greater tendency of combination even in Type I. Experimental researches together with remarks on these problems will be treated in a separate paper.

Summary.

Compound-formation in the crystalline state was found to be most closely related to the configuration, especially, to the molecular shape of the two components. Molecular compounds of different types were distinguished by the mode of compound-formation, such as the type of phase diagrams, "melting point elevation", and halochromism.

The writer wishes to express his sincere thanks to Prof. B. Kubota and to Prof. Y. Shibata of the Tokyo Imperial University for their kind guidance and encouragement throughout this study and to Dr. T. Asahina for much valuable advice. Thanks are also due to the Hattori-Hôkôkai for the grant, with the aid of which the expenses of the study were defrayed.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo
and
Kumamoto Higher Technical School.

---

(9) G. M. Bennet and G. H. Willis, *J. Chem. Soc.*, **1929**, 261.
(10) Not yet published.